PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2002-026400
(43)Date of publication of application : 25.01.2002

(51)Int.Cl. H01L 35/16
H01L 35/14
H01L 35/18
H01L 35/34
// C22C 12/00

(21)Application number : 2000-199936
(22)Date of filing : 30.06.2000

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(54) THERMOELECTRIC CONVERSION MATERIAL AND ELEMENT

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a filledskutterudite-family thermoelectric conversion material that does not contain any lead, is manufactured by a simple process where grinding and hot press are eliminated, shows high thermoelectric characteristics in a medium-temperature region of 700 K or less, and has excellent thermoelectric conversion efficiency.
SOLUTION: Current flows in an in-plain direction being vertical to the quenching direction for obtaining a material where a metal mass obtained by allowing the thermoelectric conversion material to be subjected to fluxing and quenching is heat-treated. In this case, the thermoelectric conversion material is mainly composed of a filledskutterudite compound. In the thermoelectric conversion material, the main part of the material is shown by a composition expression LnXT4Pn12. In this case, Ln is at least one kind selected from a group of La, Ce, Pr, Nd, Sm, Eu, Gd, Th, Dy, Ho, Er, Tm, Yd, Lu, Th, and U, T is at least one kind this selected from a group of Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, and Pt, Pn is at least one kind selected from a group of P, As, Sb, S, Se, and Te, and X is equal to or more than 0.2 and equal to or less than 1.

LEGAL STATUS
[Date of request for examination] 21.09.2001
[Date of sending the examiner's decision of rejection] 13.04.2004
[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]
[Date of final disposal for application]
[Patent number]
[Date of registration]
[Number of appeal against examiner's decision of rejection]
[Date of requesting appeal against examiner's decision of rejection]
[Date of extinction of right]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]
[Claim 1] the main part of an ingredient -- empirical formula LnXT4Pn12 (Ln is chosen from the group of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Th, and U -- at least -- a kind --) T that it is few as being chosen out of the group of Fe, Ru, Os, Co, Rh, Ir, nickel, Pd, and Pt A kind, Pn that it is few as being chosen out of the group of P, As, Sb, S, Se, and Te A kind, X consists of a fill DOSUKUTTERUDAITO compound shown or less [0.2 or more] by one. the remainder of an ingredient -- an empirical formula TPn2 (T is chosen from the group of Fe, Ru, Os, Co, Rh, Ir, nickel, Pd, and Pt -- at least -- a kind --) Pn is a thermoelectrical conversion ingredient with which crystal grain of the intermetallic compound which is chosen from the group of P, As, Sb, S, Se, and Te, and which is shown by kind at least is characterized by passing a current to field inboard perpendicular to said array direction in the thermoelectrical conversion ingredient which it comes to arrange in the shape of a chain.
[Claim 2] It is the thermoelectric element characterized by said p mold thermoelectrical conversion ingredient being a thermoelectrical conversion ingredient according to claim 1 in the thermoelectric element which consists of p mold thermoelectrical conversion ingredient and n mold thermoelectrical conversion ingredient which were connected electrically.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] Especially this invention relates to the thermoelectrical conversion ingredient of a fill DOSUKUTTERUDAITO system, and the thermoelectric element using it with respect to a thermoelectrical conversion ingredient and a thermoelectric element.
[0002]
[Description of the Prior Art] In recent years, the interest about the thermoelectric cooling element which used the ** RUCHIE effectiveness which is a chlorofluocarbon loess cryogenic system from the raising of consciousness to global environment problems is increasing. Moreover, similarly, in order to reduce carbon-dioxide emissions, the interest about the thermoelectric generation component using the Seebeck effect which offers the generation-of-electrical-energy system using unused waste heat energy is increasing.
[0003] The thermoelectric-cooling ingredient of p mold used for such a component and n mold and a thermoelectric generation ingredient have many which used the single crystal or polycrystal of a Bi-Te system from the height of effectiveness. Moreover, the Pb-Te system is too used for the thermoelectric material used at an elevated temperature from a room temperature for p mold and n mold from the height of effectiveness.
[0004] Pb (lead) used for the thermoelectric element used at an elevated temperature is more poisonous than a room temperature for the body -- it is harmful and is not desirable from a viewpoint of global environment problems. For this reason, in an elevated-temperature side, it is more efficient than a Pb-Te system from a room temperature until now, and empirical formula LnXT4Pn12 (Ln is chosen from the group of La, Ce, Pr, Nd, Sm, Eu, Gd, Th, and U -- at least -- a kind --) by which examination of various ingredients harmless as an ingredient is made T that it is few as being chosen out of the group of Fe, Ru, Os, Co, Rh, Ir, nickel, Pd, and Pt A kind, The fill DOSUKUTTERUDAITO compound with which Pn is chosen from the group of P, As, Sb, S, Se, and Te and in which a kind and X at least are shown or less [0.2 or more] by one The cubic structure represented with CoSb3 is shown, and there is also no toxicity (for example, J.-P. Fleurial, et al., Proc. 15th Intl. Conf. Termoelectrics, 91-95(1996).).
[0005] By the way, when alpha and resistivity are set to rho and the non-dimension performance index Z of a thermoelectrical conversion ingredient sets thermal conductivity to kappa, 2/[of ZT=alpha] rhokappa shows the Seebeck coefficient which shows the electromotive force of the thermoelectrical conversion ingredient in absolute temperature T. The property as a thermoelectrical conversion ingredient is excellent, so that the value of ZT is high.
[0006] There is an object in which the high thermoelectrical transfer characteristic of ZT>1 is shown in said fill DOSUKUTTERUDAITO compound. for example, CeFe3CoSb12 -- the compound of a presentation -- 900K ---less -- the high thermoelectrical engine performance of dimension performance-index ZT=1.4 was shown (J. -P. Fleurial, et al., Proc. 15th Intl. Conf. Termoelectrics, 91-95(1996).).
[0007] However, in order to take out a property, vacuum enclosure of the preparation powder was carried out at the quartz tube, the regulus (ingot) which it quenched after melting and was obtained was heat-treated, and the complicated production process of having carried out the

hotpress of the powder ground after cooling, and obtaining a cast was needed. There was no report of the ingredient in which the high thermoelectrical engine performance by the easy process which does not need a complicated production process called a hotpress is shown in the former.

[0008]

[Problem(s) to be Solved by the Invention] As mentioned above, fill DOSUKUTTERUDAITO known conventionally needs [it is restricted to 900K or more high temperature regions, and] a hotpress for the production process and was complicated although the large thermoelectrical conversion ingredient of the non-dimension performance index ZT with a large Seebeck coefficient was obtained.

[0009] This invention is made in view of such a problem, and aims at providing, where the regulus which quenched the big thermoelectrical conversion ingredient of the non-dimension performance index ZT after melting, and obtained it in the 700K or less degree region of moderate temperature is heat-treated using rare earth elements and a transition-metals ingredient excellent in environment nature.

[0010]

[Means for Solving the Problem] the thermoelectrical conversion ingredient of this invention -- the main part of an ingredient -- empirical formula LnXT4Pn12 (Ln is chosen from the group of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Th, and U -- at least -- a kind --) T that it is few as being chosen out of the group of Fe, Ru, Os, Co, Rh, Ir, nickel, Pd, and Pt A kind, Pn that it is few as being chosen out of the group of P, As, Sb, S, Se, and Te A kind, X consists of a fill DOSUKUTTERUDAITO compound shown or less [0.2 or more] by one. the remainder of an ingredient -- an empirical formula TPn2 (T is chosen from the group of Fe, Ru, Os, Co, Rh, Ir, nickel, Pd, and Pt -- at least -- a kind --) It is characterized by Pn passing a current to field inboard perpendicular to said array direction in the thermoelectrical conversion ingredient which the crystal grain of the intermetallic compound which is chosen from the group of P, As, Sb, S, Se, and Te, and which is shown by kind at least comes to arrange in the shape of a chain.

[0011] the organization of said thermoelectrical conversion ingredient -- empirical formula LnXT4Pn12 (Ln is chosen from the group of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Th, and U -- at least -- a kind --) T that it is few as being chosen out of the group of Fe, Ru, Os, Co, Rh, Ir, nickel, Pd, and Pt A kind, Pn that it is few as being chosen out of the group of P, As, Sb, S, Se, and Te A kind, X -- one or less [0.2 or more] -- predetermined comes out comparatively and each configuration element of the fill DOSUKUTTERUDAITO compound shown with a presentation is prepared, and after loading and carrying out vacuum suction into a vacuum housing, vacuum enclosure of the regulus which quenched the bottom of a non-oxidizing atmosphere and after the dissolution, and was obtained is carried out at a quartz tube etc., and it is heat-treated and obtained in a vacuum.

[0012] A kind of element at least chosen from the element group shown by Pn with high vapor pressure is better than the stoichiometric composition of said empirical formula in the case of said preparation to prepare mostly about 1 to 10% by weight. Moreover, if it alloys with the element of an element group beforehand shown by T when a kind of element is chosen from Gd, Tb, Dy, Ho, Er, Tm, Lu, and Th with the melting point high among the element groups shown by Ln in the case of said preparation at least, it will become easy to attain the stoichiometric composition of said target empirical formula.

[0013] Although the high vacuum of 5x10 - 3 or less Pa is desirable, if the vacuum suction before the time of the dissolution is the degree of vacuum of 10 - 5 or more Pa, it is enough. Moreover, although gas, such as Ar of 99.99% or more of high grade and helium, has desirable purity, if the non-oxidizing atmosphere at the time of the dissolution is 99.9999% or less of purity, it is enough. In case vacuum enclosure of the regulus obtained by dissolving is carried out at a quartz tube etc., the high vacuum of 5x10 - 3 or less Pa is desirable. If it may be able to do, the high vacuum of 5x10 - 4 or less Pa is desirable, but it is enough if it is the degree of vacuum of 10 - 5 or more Pa. Each vacuum ambient atmosphere mentioned above is carried out in order to prevent oxidation of said thermoelectrical conversion ingredient.

[0014] In addition, as a solution process accompanied by quenching, although an arc solution

process is mentioned, the so-called single rolling method for injecting and quenching on the metal drum front face where the heat capacity which is rotating the molten metal after the RF dissolution is large besides the arc dissolution, or the congruence rolling method may be used.
[0015] Although the temperature requirement of heat treatment among a vacuum depends also on a presentation, 873K-1023K are desirable. If lower than 873K, a reaction will not progress, but if higher than 1023K, the phase which is not desirable will appear on a property. Heat treatment time amount has 5 desirable hours or more. Although it depends also on temperature, a reaction does not progress in case of time amount shorter than 5 hours. Moreover, the processing time longer than 100 hours is not practical.
[0016] As for the ratio of the remainder shown with said empirical formula TPn2, it is [in / to the whole ingredient including the main part of the ingredient shown by said empirical formula LnXT4Pn12 / the cross-section organization of the quenching direction of said regulus] desirable that it is 10% or less of rate of surface ratio. If 10% is exceeded, the thermoelectrical property as the whole ingredient will fall. Although 5% or less of ratio is desirable if it may be able to do, what is necessary is just 1% or more of ratio. Thermoelectrical property sufficient as the whole ingredient can be desired.
[0017] There may not be the need that the chain-like array of the intermetallic-compound crystal grain shown with said empirical formula TPn2 is continuing, and may be discontinuous in the shape of an island. Spacing of crystal grain may not be fixed. What is necessary is just to be able to specify an array in the quenching direction on pattern recognition in the cross-section organization of the quenching direction of said regulus.
[0018] The direction which passes a current should just be in a field perpendicular to said array direction. Moreover, if another expression is carried out, what is necessary is just in a field perpendicular to the quenching direction of said regulus. In addition, even if it does not need to be correctly perpendicular and leans in plus or the range of 15 minus, sufficient thermoelectrical property can be desired.
[0019] Next, in the thermoelectric element which the thermoelectric element of this invention turns into from p mold thermoelectrical conversion ingredient and n mold thermoelectrical conversion ingredient which were connected electrically, said p mold thermoelectrical conversion ingredient is characterized by being the thermoelectrical conversion ingredient of p mold which is the thermoelectrical conversion ingredient of this invention.
[0020] In addition, what is necessary is just to use known ingredients, such as Bi2(Te, Se) 3, Co0.97Ir0.03Sb2.81Te0.04As 0.15, and (Pd0.03Co0.97) Sb3, as an n mold thermoelectrical conversion ingredient.
[0021] The end of p mold thermoelectrical conversion ingredient is connected through as common an electrode as the end of n mold thermoelectrical conversion ingredient, and, as for the other end of each thermoelectrical conversion ingredient, the electrode according to individual is formed. An electrical potential difference occurs between p mold thermoelectrical conversion ingredient and n mold thermoelectrical conversion ingredient by heating a common electrode to an elevated temperature, cooling the electrode according to individual, and distinguishing between each thermoelectrical conversion ingredient edge. Consequently, if resistance is connected between the electrodes according to individual, a current can flow and power can be taken out.
[0022]
[Embodiment of the Invention] The thermoelectrical conversion ingredient of this invention is explained below at a detail using an example.
(Example 1) After it prepared each configuration element shown by empirical formula Ce0.9Fe3CoSb12 so that Sb might increase more than a predetermined rate 3% by weight, and it loaded with it Haas made from Cu to whom water cooling of [in an arc furnace] is carried out and it carried out vacuum suction to the degree of vacuum of 2x10 to 3 Pa, the high grade Ar of 99.999% of purity was introduced to -0.04MPa, it was made the reduced pressure Ar ambient atmosphere, and the arc dissolution was carried out. Vacuum enclosure was carried out by the high vacuum of ten to 4 Pa at the quartz tube, and the regulus quenched and obtained after the dissolution by Haas made from Cu by which water cooling is carried out was heat-treated by

973K for 30 hours.
[0023] When a part of obtained regulus was ground and having been investigated with the X-ray diffraction method, it turned out that it is mainly concerned with the phase of the same cubic structure as the fill DOSUKUTTERUDAITO compound represented with CoSb3, and the phase of the same structure as little Sb2Fe is included.
[0024] Next, it was checked that the place which gazed at the cross-section organization of the quenching direction of a regulus in SEM, and the different-species phase with much Fe deposit in the shape of an island in the quenching direction. The rate of surface ratio of a different-species phase with much Fe was 3% to the whole cross section.
[0025] Moreover, it checked that they were the place which analyzed the presentation of the obtained regulus by ICP emission spectrometry, and an almost predetermined presentation.
[0026] The various test samples which have the measurement direction in a field perpendicular to the quenching direction of a regulus were extracted. the thermal diffusivity according to an optical alternating current anodizing process Seebeck coefficient alpha which prepares a temperature gradient in resistivity rho and both ends by 4 terminal method, measures electromotive force, and is obtained, and in order to ask for thermal conductivity kappa further, the specific heat by differential scanning calorimeter measurement, and Archimedes -- each measurement of the consistency by law was performed in 300K to 700K, and it asked for the non-dimension performance index ZT (Z=alpha 2 rho/kappa) from these results. A result is shown in Table 1.
(An example 2 thru/or example 7) La0.5Fe3CoSb12, YbFe3CoSb12, PrOs2Rh2Sb12, NdFe2nickel2As12, and each configuration element shown with each empirical formula of La0.5Ru4P12 were prepared so that Sb, As, and P might increase more than a predetermined rate 3% by weight, and the arc dissolution was carried out like the example 1. By 973K, vacuum heat treatment was carried out by 973K 923K, and carried [for 30 hours / for 50 hours] it out by 873K 900K for 30 hours for 30 hours for 70 hours, respectively.
[0027] Moreover, the alloy of the predetermined ratio obtained by carrying out the arc dissolution of Er and the Fe like an example 1 beforehand among each configuration element shown with the empirical formula of ErFe4Sb12 was prepared so that Sb might increase more than a predetermined rate 3% by weight, and the arc dissolution was carried out like the example 1. Vacuum heat treatment was carried out by 873K for 80 hours.
[0028] The result of having asked for the non-dimension performance index ZT of the obtained regulus like the example 1 is written together to Table 1.
[Table 1]

	試料組成	無次元性能指数ＺＴ	温度Ｔ／Ｋ
実施例１	$Ce_{0.9}Fe_3CoSb_{12}$	１．０	６００
実施例２	$La_{0.5}Fe_3CoSb_{12}$	０．９	６００
実施例３	$YbFe_3CoSb_{12}$	１．０	６５０
実施例４	$PrOs_2Rh_2Sb_{12}$	０．９	６８０
実施例５	$NdFe_2Ni_2As_{12}$	０．８	７００
実施例６	$La_{0.5}Ru_4P_{12}$	０．８	７００
実施例７	$ErFe_4Sb_{12}$	０．９	６９０
比較例１	$YbFe_3CoSb_{12}$	０．４	７００

(Example 1 of a comparison) The various test samples which have the measurement direction in the field of the quenching direction of the regulus obtained in the example 3 were extracted. the thermal diffusivity according to an optical alternating current anodizing process Seebeck coefficient alpha which prepares a temperature gradient in resistivity rho and both ends by 4

terminal method, measures electromotive force, and is obtained, and in order to ask for thermal conductivity kappa further, the specific heat by differential scanning calorimeter measurement, and Archimedes -- each measurement of the consistency by law was performed in 300K to 700K, and it asked for the non-dimension performance index ZT from these results. The result is written together to Table 1.

[0029] An example and the example 1 of a comparison show that the thermoelectrical property of a sample of having the measurement direction is high in a field perpendicular to the quenching direction of a regulus.

[0030]

[Effect of the Invention] As explained above, according to this invention, in the sample of the fill DOSUKUTTERUDAITO system in the condition of having heat-treated the regulus which it quenched after melting and was obtained, the thermoelectrical conversion ingredient in which a high thermoelectrical property is shown in the 700K or less degree region of moderate temperature is obtained by passing a current to field inboard perpendicular to the quenching direction.

[Translation done.]

(19)日本国特許庁（ＪＰ）　(12) **公開特許公報**（Ａ）　(11)特許出願公開番号
特開2002－26400
（P2002－26400A）
(43)公開日　平成14年１月25日(2002.1.25)

(51)Int.Cl.[7]	識別記号	ＦＩ	テーマコード（参考）
Ｈ０１Ｌ　35/16		Ｈ０１Ｌ　35/16	
35/14		35/14	
35/18		35/18	
35/34		35/34	
// Ｃ２２Ｃ　12/00		Ｃ２２Ｃ　12/00	

審査請求　有　　請求項の数２　ＯＬ　（全４頁）

(21)出願番号　特願2000－199936(P2000－199936)

(22)出願日　平成12年６月30日(2000.6.30)

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(54)【発明の名称】　熱電変換材料および熱電変換素子

(57)【要約】
【課題】　鉛を含まないフィルドスクッテルダイト系の熱電変換材料であって、粉砕・ホットプレスを省略した簡単な製造工程で、７００Ｋ以下の中温度域で高い熱電特性を示す、高熱電変換効率の熱電変換材料の提供。
【解決手段】　材料の主たる部分が、組成式ＬｎＸＴ４Ｐｎ１２（ＬｎはＬａ，Ｃｅ，Ｐｒ，Ｎｄ，Ｓｍ，Ｅｕ，Ｇｄ，Ｔｂ，Ｄｙ，Ｈｏ，Ｅｒ，Ｔｍ，Ｙｂ，Ｌｕ，Ｔｈ，Ｕの群から選ばれる少なくとも一種、ＴはＦｅ，Ｒｕ，Ｏｓ，Ｃｏ，Ｒｈ，Ｉｒ，Ｎｉ，Ｐｄ，Ｐｔの群から選ばれる少なくとも一種、ＰｎはＰ，Ａｓ，Ｓｂ，Ｓ，Ｓｅ，Ｔｅの群から選ばれる少なくとも一種、Ｘは０．２以上１以下）で示されるフィルドスクッテルダイト化合物を主とする熱電変換材料を溶融後急冷して得た金属塊を熱処理した材料を、急冷方向に垂直な面内方向に電流を流す事により得られる。

【特許請求の範囲】
【請求項１】　材料の主たる部分が、組成式ＬｎＸＴ４Ｐｎ１２（ＬｎはＬａ，Ｃｅ，Ｐｒ，Ｎｄ，Ｓｍ，Ｅｕ，Ｇｄ，Ｔｂ，Ｄｙ，Ｈｏ，Ｅｒ，Ｔｍ，Ｙｂ，Ｌｕ，Ｔｈ，Ｕの群から選ばれる少なくとも一種、ＴはＦｅ，Ｒｕ，Ｏｓ，Ｃｏ，Ｒｈ，Ｉｒ，Ｎｉ，Ｐｄ，Ｐｔの群から選ばれる少なくとも一種、ＰｎはＰ，Ａｓ，Ｓｂ，Ｓ，Ｓｅ，Ｔｅの群から選ばれる少なくとも一種、Ｘは０．２以上１以下）で示されるフィルドスクッテルダイト化合物からなり、材料の残部が、組成式ＴＰｎ２（ＴはＦｅ，Ｒｕ，Ｏｓ，Ｃｏ，Ｒｈ，Ｉｒ，Ｎｉ，Ｐｄ，Ｐｔの群から選ばれる少なくとも一種、ＰｎはＰ，Ａｓ，Ｓｂ，Ｓ，Ｓｅ，Ｔｅの群から選ばれる少なくとも一種）で示される金属間化合物の結晶粒が連鎖状に配列してなる熱電変換材料に於いて、前記配列方向に垂直な面内方向に電流を流すことを特徴とする熱電変換材料。
【請求項２】　電気的に接続されたｐ型熱電変換材料およびｎ型熱電変換材料からなる熱電変換素子において、前記ｐ型熱電変換材料は、請求項１記載の熱電変換材料であることを特徴とする熱電変換素子。
【発明の詳細な説明】
【０００１】
【発明の属する技術分野】本発明は、熱電変換材料および熱電変換素子に係わり、特にフィルドスクッテルダイト系の熱電変換材料およびそれを用いた熱電変換素子に関する。
【０００２】
【従来の技術】近年、地球環境問題に対する意識の高揚から、フロンレス冷却機器であるペルチェ効果を利用した熱電冷却素子に関する関心が高まっている。また、同じく、二酸化炭素排出量を削減するために、未利用廃熱エネルギーを使った発電システムを提供する、ゼーベック効果を利用した熱電発電素子に対する関心が高まっている。
【０００３】このような素子に用いるｐ型、ｎ型の熱電冷却材料、熱電発電材料は、効率の高さから、Ｂｉ－Ｔｅ系の単結晶または多結晶を使用したものが多い。また、室温より高温で使用される熱電材料には、やはり効率の高さから、ｐ型、ｎ型共にＰｂ－Ｔｅ系が用いられている。
【０００４】室温より高温で使用される熱電変換素子に用いられているＰｂ（鉛）は人体にとって有毒有害であり、また地球環境問題の観点からも好ましくない。このため、室温より高温側では、これまでＰｂ－Ｔｅ系より高効率で、かつ材料として無害な各種材料の検討がなされている組成式ＬｎＸＴ４Ｐｎ１２（ＬｎはＬａ，Ｃｅ，Ｐｒ，Ｎｄ，Ｓｍ，Ｅｕ，Ｇｄ，Ｔｈ，Ｕの群から選ばれる少なくとも一種、ＴはＦｅ，Ｒｕ，Ｏｓ，Ｃｏ，Ｒｈ，Ｉｒ，Ｎｉ，Ｐｄ，Ｐｔの群から選ばれる少なくとも一種、ＰｎはＰ，Ａｓ，Ｓｂ，Ｓ，Ｓｅ，Ｔｅの群から選ばれる少なくとも一種、Ｘは０．２以上１以下）で示されるフィルドスクッテルダイト化合物は、ＣｏＳｂ３で代表される立方晶構造を示し、毒性もない（例えば、Ｊ．－Ｐ．　Ｆｌｅｕｒｉａｌ，ｅｔ　ａｌ．，Ｐｒｏｃ．　１５ｔｈ　Ｉｎｔｌ．　Ｃｏｎｆ．　Ｔｅｒｍｏｅｌｅｃｔｒｉｃｓ，　９１－９５（１９９６）．）。
【０００５】ところで、熱電変換材料の無次元性能指数Ｚは、絶対温度Ｔにおける熱電変換材料の起電力を示すゼーベック係数をα、抵抗率をρ、熱伝導率をκとした時、$ZT=\alpha^2/\rho\kappa$で示される。ＺＴの値が高いほど熱電変換材料としての特性が優れる。
【０００６】前記フィルドスクッテルダイト化合物には、ＺＴ＞１という高い熱電変換特性を示す物がある。例えば、ＣｅＦｅ３ＣｏＳｂ１２なる組成の化合物は、９００Ｋで無次元性能指数ＺＴ＝１．４という高い熱電性能を示した（Ｊ．－Ｐ．　Ｆｌｅｕｒｉａｌ，ｅｔ　ａｌ．，Ｐｒｏｃ．　１５ｔｈ　Ｉｎｔｌ．　Ｃｏｎｆ．　Ｔｅｒｍｏｅｌｅｃｔｒｉｃｓ，　９１－９５（１９９６）．）。
【０００７】しかしながら、特性を出すためには、調合粉末を石英管に真空封入し、溶融後急冷して得た金属塊（インゴット）を熱処理し、冷却後粉砕した粉末をホットプレスして成型品を得るという煩雑な製造工程を必要としていた。ホットプレスという煩雑な製造工程を必要としない、簡単な製法による高い熱電性能を示す材料の報告は、従来にはなかった。
【０００８】
【発明が解決しようとする課題】上述したように、従来知られるフィルドスクッテルダイトは、ゼーベック係数が大きく無次元性能指数ＺＴの大きい熱電変換材料が得られるものの、９００Ｋ以上の高温度域に限られ、また、その製造工程にホットプレスを必要とし煩雑であった。
【０００９】本発明は、このような問題に鑑みてなされたものであり、環境性に優れた希土類元素と遷移金属材料を用い、７００Ｋ以下の中温度域で無次元性能指数ＺＴの大きな熱電変換材料を、溶融後急冷して得た金属塊を熱処理した状態で提供することを目的とする。
【００１０】
【課題を解決するための手段】本発明の熱電変換材料は、材料の主たる部分が、組成式ＬｎＸＴ４Ｐｎ１２（ＬｎはＬａ，Ｃｅ，Ｐｒ，Ｎｄ，Ｓｍ，Ｅｕ，Ｇｄ，Ｔｂ，Ｄｙ，Ｈｏ，Ｅｒ，Ｔｍ，Ｙｂ，Ｌｕ，Ｔｈ，Ｕの群から選ばれる少なくとも一種、ＴはＦｅ，Ｒｕ，Ｏｓ，Ｃｏ，Ｒｈ，Ｉｒ，Ｎｉ，Ｐｄ，Ｐｔの群から選ばれる少なくとも一種、ＰｎはＰ，Ａｓ，Ｓｂ，Ｓ，Ｓｅ，Ｔｅの群から選ばれる少なくとも一種、Ｘは０．２以上１以下）で示されるフィルドスクッテルダイ

ト化合物からなり、材料の残部が、組成式ＴＰｎ２（ＴはＦｅ，Ｒｕ，Ｏｓ，Ｃｏ，Ｒｈ，Ｉｒ，Ｎｉ，Ｐｄ，Ｐｔの群から選ばれる少なくとも一種、ＰｎはＰ，Ａｓ，Ｓｂ，Ｓ，Ｓｅ，Ｔｅの群から選ばれる少なくとも一種）で示される金属間化合物の結晶粒が連鎖状に配列してなる熱電変換材料に於いて、前記配列方向に垂直な面内方向に電流を流すことを特徴とする。

【００１１】前記熱電変換材料の組織は、組成式ＬｎＸＴ４Ｐｎ１２（ＬｎはＬａ，Ｃｅ，Ｐｒ，Ｎｄ，Ｓｍ，Ｅｕ，Ｇｄ，Ｔｂ，Ｄｙ，Ｈｏ，Ｅｒ，Ｔｍ，Ｙｂ，Ｌｕ，Ｔｈ，Ｕの群から選ばれる少なくとも一種、ＴはＦｅ，Ｒｕ，Ｏｓ，Ｃｏ，Ｒｈ，Ｉｒ，Ｎｉ，Ｐｄ，Ｐｔの群から選ばれる少なくとも一種、ＰｎはＰ，Ａｓ，Ｓｂ，Ｓ，Ｓｅ，Ｔｅの群から選ばれる少なくとも一種、Ｘは０．２以上１以下）なる組成で示されるフィルドスクッテルダイト化合物の各構成元素を所定の割合で調合し、真空容器内に装填して真空引きした後、非酸化性雰囲気下、溶解後急冷して得られた金属塊を石英管等に真空封入し、真空中で熱処理して得られる。

【００１２】前記調合の際、蒸気圧の高いＰｎで示される元素群から選ばれる少なくとも一種の元素は、前記組成式の化学量論組成より重量で約１～１０％多く調合すると良い。また、前記調合の際、Ｌｎで示される元素群の内、融点が高いＧｄ，Ｔｂ，Ｄｙ，Ｈｏ，Ｅｒ，Ｔｍ，Ｌｕ，Ｔｈから少なくとも一種の元素が選ばれる場合は、予めＴで示される元素群の元素と合金化しておくと、目標とする前記組成式の化学量論組成を達成しやすくなる。

【００１３】溶解時に先立つ真空引きは、５×１０－３Ｐａ以下の高真空が望ましいが、１０－５Ｐａ以上の真空度であれば充分である。また、溶解時の非酸化性雰囲気は、純度が９９．９９％以上の高純度のＡｒ，Ｈｅ等のガスが望ましいが、９９．９９９９％以下の純度であれば充分である。溶解して得られた金属塊を石英管等に真空封入する際は、５×１０－３Ｐａ以下の高真空が望ましい。でき得れば５×１０－４Ｐａ以下の高真空が望ましいが、１０－５Ｐａ以上の真空度であれば充分である。上述した真空雰囲気は、いずれも前記熱電変換材料の酸化を防ぐ目的で実施される。

【００１４】尚、急冷を伴う溶解法としては、アーク溶解法が挙げられるが、アーク溶解以外にも、高周波溶解後に溶湯を回転している熱容量の大きい金属ドラム表面に射出して急冷する、所謂、単ロール法、または、双ロール法でも良い。

【００１５】真空中熱処理の温度範囲は、組成にも拠るが、８７３Ｋ～１０２３Ｋが望ましい。８７３Ｋより低いと反応が進まず、１０２３Ｋより高いと特性上望ましくない相が出現する。熱処理時間は５時間以上が望ましい。温度にも拠るが、５時間より短い時間だと反応が進まない。また、１００時間より長い処理時間は実用的ではない。

【００１６】前記組成式ＴＰｎ２で示される残部の比率は、前記組成式ＬｎＸＴ４Ｐｎ１２で示される材料の主たる部分を含めた材料全体に対して、前記金属塊の急冷方向の断面組織に於いて１０％以下の面積比率であることが望ましい。１０％を越えると、材料全体としての熱電特性が低下する。でき得れば５％以下の比率が望ましいが、１％以上の比率であれば良い。材料全体として充分な熱電特性が望める。

【００１７】前記組成式ＴＰｎ２で示される金属間化合物結晶粒の連鎖状配列は、連続している必要性はなく、島状に不連続であってよい。結晶粒の間隔は、一定でなくてよい。前記金属塊の急冷方向の断面組織に於いて、パターン認識上、急冷方向に配列が特定できれば良い。

【００１８】電流を流す方向は、前記配列方向に垂直な面内であればよい。また、別な表現をすれば、前記金属塊の急冷方向に垂直な面内であればよい。なお、正確に垂直である必要はなく、プラス、または、マイナス１５度の範囲で傾いていても、充分な熱電特性が望める。

【００１９】次に、本発明の熱電変換素子は、電気的に接続されたｐ型熱電変換材料およびｎ型熱電変換材料からなる熱電変換素子において、前記ｐ型熱電変換材料は、本発明の熱電変換材料であるｐ型の熱電変換材料であることを特徴とする。

【００２０】尚、ｎ型熱電変換材料としては、Ｂｉ２（Ｔｅ，Ｓｅ）３、Ｃｏ０．９７Ｉｒ０．０３Ｓｂ２．８１Ｔｅ０．０４Ａｓ０．１５、及び（Ｐｄ０．０３Ｃｏ０．９７）Ｓｂ３などの既知の材料を使用すればよい。

【００２１】ｐ型熱電変換材料の一端はｎ型熱電変換材料の一端と共通の電極を介して接続されており、それぞれの熱電変換材料の他端は個別の電極が形成されている。共通の電極を高温に加熱し、個別の電極を冷却して、それぞれの熱電変換材料端部に温度差をつけることで、ｐ型熱電変換材料とｎ型熱電変換材料との間に電圧が発生する。その結果、個別の電極の間に抵抗を接続すると電流が流れ、電力を取り出すことができる。

【００２２】

【発明の実施の形態】本発明の熱電変換材料について、実施例を用いて以下に詳細に説明する。

（実施例１）組成式Ｃｅ０．９Ｆｅ３ＣｏＳｂ１２で示される各構成元素を、Ｓｂが所定の割合より重量で３％多くなるように調合し、アーク炉内の水冷されているＣｕ製のハースに装填して、２×１０－３Ｐａの真空度まで真空引きした後、純度９９．９９９％の高純度Ａｒを－０．０４ＭＰａまで導入して減圧Ａｒ雰囲気にして、アーク溶解した。溶解後、水冷されているＣｕ製のハースで急冷して得られた金属塊を、石英管に１０－４Ｐａの高真空で真空封入し、９７３Ｋで３０時間熱処理した。

【００２３】得られた金属塊の一部を粉砕しＸ線回折法にて調べたところ、ＣｏＳｂ３で代表されるフィルドスクッテルダイト化合物と同じ立方晶構造の相を主とし、少量のＳｂ２Ｆｅと同じ構造の相を含むことが分かった。

【００２４】次に、金属塊の急冷方向の断面組織をＳＥＭにて観察した所、Ｆｅの多い異種相が急冷方向に島状に析出しているのが確認された。Ｆｅの多い異種相の面積比率は、断面全体に対して３％であった。

【００２５】また、得られた金属塊の組成をＩＣＰ発光分光法で分析した所、ほぼ所定の組成になっているのを確認した。

【００２６】金属塊の急冷方向に垂直な面内に測定方向を有する各種測定用試料を採取した。４端子法にて抵抗率ρ、両端に温度差を設け起電力を測定して得られるゼーベック係数α、さらに、熱伝導率κを求めるため、光交流法による熱拡散率、示差走査熱量計測定による比熱、アルキメデス法による密度の各測定を、３００Ｋから７００Ｋの範囲で行い、これらの結果から無次元性能指数ＺＴ（$Z=\alpha^2\rho/\kappa$）を求めた。結果を表１に示す。

（実施例２乃至実施例７）$La_{0.5}Fe_3CoSb_{12}$、$YbFe_3CoSb_{12}$、$PrOs_2Rh_2Sb_{12}$、$NdFe_2Ni_2As_{12}$、$La_{0.5}Ru_4P_{12}$の各組成式で示される各構成元素を、Ｓｂ、Ａｓ、Ｐが所定の割合より重量で３％多くなるように調合し、実施例１と同様にアーク溶解した。真空熱処理は、それぞれ、９７３Ｋで３０時間、９７３Ｋで５０時間、９２３Ｋで７０時間、９００Ｋで３０時間、８７３Ｋで３０時間実施した。

【００２７】また、$ErFe_4Sb_{12}$の組成式で示される各構成元素の内、予めＥｒとＦｅを実施例１と同様にアーク溶解して得られる所定比の合金を、Ｓｂが所定の割合より重量で３％多くなるように調合し、実施例１と同様にアーク溶解した。真空熱処理は、８７３Ｋで８０時間実施した。

【００２８】得られた金属塊の無次元性能指数ＺＴを、実施例１と同様にして求めた結果を表１に併記する。

【表１】

	試料組成	無次元性能指数ＺＴ	温度Ｔ／Ｋ
実施例１	$Ce_{0.9}Fe_3CoSb_{12}$	１．０	６００
実施例２	$La_{0.5}Fe_3CoSb_{12}$	０．９	６００
実施例３	$YbFe_3CoSb_{12}$	１．０	６５０
実施例４	$PrOs_2Rh_2Sb_{12}$	０．９	６８０
実施例５	$NdFe_2Ni_2As_{12}$	０．８	７００
実施例６	$La_{0.5}Ru_4P_{12}$	０．８	７００
実施例７	$ErFe_4Sb_{12}$	０．９	６９０
比較例１	$YbFe_3CoSb_{12}$	０．４	７００

（比較例１）実施例３で得られた金属塊の、急冷方向の面内に測定方向を有する各種測定用試料を採取した。４端子法にて抵抗率ρ、両端に温度差を設け起電力を測定して得られるゼーベック係数α、さらに、熱伝導率κを求めるため、光交流法による熱拡散率、示差走査熱量計測定による比熱、アルキメデス法による密度の各測定を、３００Ｋから７００Ｋの範囲で行い、これらの結果から無次元性能指数ＺＴを求めた。その結果を表１に併記する。

【００２９】実施例および比較例１から、金属塊の急冷方向に垂直な面内に測定方向を有する試料の熱電特性が高いことが分かる。

【００３０】

【発明の効果】以上説明したように本発明によれば、溶融後急冷して得た金属塊を熱処理した状態のフィルドスクッテルダイト系の試料において、急冷方向に垂直な面内方向に電流を流す事により、７００Ｋ以下の中温度域で高い熱電特性を示す熱電変換材料が得られる。